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RAMAN EFFECT IN BORIC ACID AND IN SOME BORON COMPOUNDS

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Plate I

ABSTRACT. The paper gives the results obtained from the author's investigations on Raman effect in boric acid and other borates. In the case of the boric acid solution the frequencies 515, 874 and 986 cm^{-1} and in the case of the solid powder the frequency 882 cm.$^{-1}$ in addition of the two broad lines at 3195 and 3290 cm^{-1} due to the vibrations of O-H, were observed. Presumably therefore the molecule $B(OH)_3$ has a symmetry D_{3h}.

The results obtained in the case of methyl borate, ethyl borate and butyl borate are also included in the report.

INTRODUCTION

In continuation of our investigations on the Raman effect in organic and inorganic compounds [1] very recently we studied the Raman spectra of boric acid and of a few boron compounds. The present paper gives the report of the same.

EXPERIMENTAL ARRANGEMENT

The substances were studied either in solid and liquid states or in solution and they were all Merck's or Kahlbaum's preparation further purified in the usual way. The method of illumination was virtually the same as that of Wood in the case of the liquids and the solutions. The liquid (or the solution) was put in the inner tube placed inside the outer jacket of the Wood's tube. The whole was clamped upright and a vertical mercury arc lamp was placed alongside, so that the light scattered at right angles emerged along the axis of the vertical tube. The scattered beam was totally reflected by a total reflection prism on to the slit of the spectrograph thereby making the maximum possible illumination. The slit of the spectrograph was guarded from direct illumination by screens and practically the whole light that entered the slit was due to the scattering at right angles.

At the ordinary temperature cold water was continually circulated through the annular space and at the higher temperature hot water from a jar was continually made to pass by a small pump, and two thermometers at the inlet and at the outlet measured the temperature. The continuous band of the exciting light was cut off by adding a little fluorescein to this circulating water.

The plates were all measured with a Hilger travelling microscope and the wave-lengths of the Raman lines calculated by the well-known formula $\lambda = \lambda_0 \left(\frac{1}{n - n_0} \right)$, with the known mercury lines taken as standard. In the case of some of the plates copper lines were taken as standard.

In the case of the solid powder the usual technique of the complementary colour filters was employed.

RESULTS IN DISCUSSIONS

Boric Acid :- Many workers tried to investigate this compound in solution but the intense continuous band due to the fluorescence of the substance stood in their way. Ananthakrishnan [2] while investigating a few boron compounds found only one frequency at 875 cm.$^{-1}$ in the case of the saturated solution of the acid. In our present investigation we also observed this continuous band, which was so strong that it practically obliterated the faint Raman lines. But as in the case of phosphoric acid observed by Hibben,[3] in arsenates and glycerine observed by the present author [4] and in the amino acids observed by Wright and Lee,[5] it was found that the addition of KI to the solution removed this band to a considerable extent. The results of our measurements are given in the following table and in plate I. It will be evident from the table that we have observed the following frequencies, *viz.*, $\Delta\nu$ = 515, 872, 986 cm.$^{-1}$ in the case of the saturated solution of the acid.

The spectrum of the powdered solid shows a strong line at $\Delta\nu$ = 882 cm.$^{-1}$, the other lines found in the case of the solution could not be identified owing to the continuous band. In addition to the aforesaid line there are two broad lines at $\Delta\nu$ = 3195 and 3290 cm.$^{-1}$

TABLE I

Raman frequencies in Boric Acid, $HO\text{-}B\langle^{OH}_{OH}$

Substance	Cm.$^{-1}$		
Boric Acid sol. saturated at 70°C	515 w	872 s	986 w
Boric acid solid	882 s	3195 bs	3290 bs

s—strong, w—weak, b—broad.

We might consider the molecule of the boric acid to be analogous to the general type of molecule XY_3, provided we treat the group OH as a single unit. Such a molecule can have two types of symmetry C_{3v} or D_{3h} according as the structure is pyramidal or coplaner. The symmetric plane structure possesses four vibrations, one totally symmetric vibration which is active in Raman effect but inactive in infra-red, one asymmetric with respect to the plane of the molecule and active in infra-red but inactive in the Raman spectrum, and two doubly degenerate vibrations which are active both in Raman spectrum and in the infra-red. In all, we expect three frequencies in the case of the coplaner structure. These vibrations are 515, 872 and 686 cm.$^{-1}$ in the case of the boric acid and hence the acid has the symmetry D_{3h}.

Another interesting fact is revealed in the table, *viz.*, the frequency 872 in the case of the saturated solution which is due to the totally symmetrical vibration of the molecule $B(OH)_3$ becomes 882 in the case of the solid. Such an increase has also been found by others in the cases of many organic and inorganic substances. As for the vibrations 3195 and 3200 cm.$^{-1}$ observed in the case of the powder, they perhaps owe their origin to the vibrations of O-H.

ORGANIC BORATES

In this connection we investigated a few organic borates, the results obtained are tabulated in the following table II. The figures within the brackets indicate the intensities.

TABLE II

Methyl borate.	Ethyl borate	Butyl borate
201 (6)	240 (1)	
	295 (2)	
318 (4)	340 (1)	478 (1)
521 (2)		7[illegible] (1)
726 (10)	727 (6)	739 (1)
	750 (1)	
	809 (1)	829 (6)
854 (0)	890 (4)	
	947 (2)	900 (2)
		965 (3)

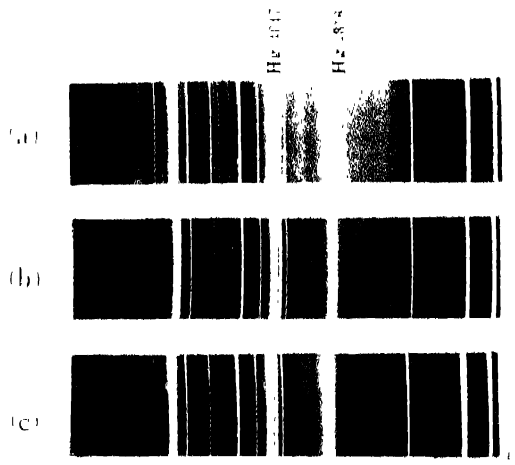
TABLE II (*contd.*)

Methyl borate.	Ethyl borate.	Butyl borate.
1028 (5)	1050 (4)	1065 (4)
1061 (1)	1090 (5)	
1112 (2)		
	1280 (1)	1258 (4)
	1328 (1)	1315 (1)
	1390 (1)	1340 (6)
	1446 (8)	1450 (8)
1460 (5b)	1486 (2)	
	2864 (8)	2858 (8)
2836 (1)	2898 (8)	2880 (6)
2875 (12)		
2910 (2)	2932 (10)	2940 (8)
2940 (9)		2970 (8)
2975 (4)		
2986 (5b)		
	3046 (6)	

It might be mentioned here that the Raman spectra of a few organic borates were investigated by Joglekar and Thatte[6] a few years ago and very recently Ananthakrishna[7] also studied the Raman spectra of methyl and ethyl borates. But there is a great disagreement between them as will be evident from the table III where the values for the methyl and ethyl borates obtained by Joglekar and Thatte and Ananthakrishnan, together with those observed by the present author are given.

TABLE III.

Methyl borate.			Ethyl borate.		
Author.	J & T.	Anantha.	Author.	J & T.	Anantha.
201		197	240	240	242
			295	273	295
318		318	340	323	350
521	488	526		405	413
				557	531
				615	



Raman Spectra of Boric Acid.

(*a*) Solution, saturated at 70°C without potassium iodide

(*b*) Solution saturated at 30°C with potassium iodide.

(*c*) Solution, saturated at 70°C with potassium iodide.

TABLE III (*contd.*).

Methyl borate.			Ethyl borate.		
Author.	J & T	Anantha	Author	J & T.	Anantha
726	710	728	727	722	727
			750		
			800	855	800
851	860		890	890	892
			917	911	917
1028	1028	1030	1050	1055	1050
1001			1000		1002
1112	1112	1171		1113	
				1160	
				1210	
			1280	1280	1280
			1335	1335	1328
			1300		1300
1400	1450	1460	1440	1457	1440
			1486		1485
	1563				
	1753			1820	
				1807	
	1950				
	2038				
2830		2833	2861		2864
2875	2898	2870	2905		2908
2910		2910			
2940	2940	2940	2932	2930	2932
2975		2975		2977	2975
2986		2988			
	3020		3046	3040	
				3118	

We might also consider the molecules of methyl borate $B(OCH_3)_3$ as analogous to the general type XY_3, provided we treat the group OCH_3 as a single unit. Such a molecule can have, as we have already mentioned, two types of

symmetry C_{3v} and D_{3h} according as the structure is pyramidal or coplaner. In the former case, "C_{3v}," there should be two totally symmetric and two double degernate vibrations, all the four being active in the Raman spectrum. These four frequencies are identified to be 210, 318, 521 and 726 cm.$^{-1}$ in the case of the methyl borate, which consequently has the symmetry "C_{3v}." Of the other frequencies, 1028 and 1112 cm.$^{-1}$ are probably due to the vibrations of $-OCH_3$ group and the remaining frequencies are to be ascribed to the hydrogen atoms.

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